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(54) THERMOPLASTIC POLYESTER MOULDING COMPOSITIONS

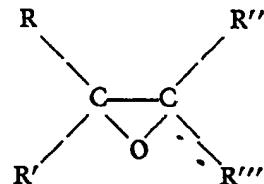
(71) We, FARBWERKE HOECHST AKTIENGESELLSCHAFT vormals Meister Lucius & Brüning, a Body Corporate recognised under German Law, of 6230 Frankfurt-5 Main 80, P.O. Box 800320, Federal Republic of Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described 10 in and by the following statement:—

The present invention relates to thermoplastic compositions based on polyesters and their use in injection-moulding. It is known that polyethylene terephthalate can be processed, under controlled conditions, into crystalline shaped articles by injection-moulding. In this process, the polyester raw material is required to have, above all, a sufficiently high molecular weight, and a crystallization 15 promoting agent has to be added, since pure polyethylene terephthalate crystallizes only slowly. Crystallization may also be accelerated by other techniques during the injection-moulding process, for example, by heating the 20 mould to a temperature from 130°C to 150°C. Numerous additives, mostly of a mineral character, which serve to accelerate crystallization, have been described. The addition of these 25 compounds and the heating of the mould guarantee a technically suitable rate of crystallization in the mould. Another problem in the injection-moulding process of thermoplastic 30 polyester compositions is in the removal of the shaped articles from the mould. Even well 35 crystallized shaped articles frequently adhere strongly to the walls of the mould. This difficulty of removal, which is further intensified by the necessary heating of the mould, jeopardizes the economy of the process.

40 The present invention provides a process for the production of a crystalline thermoplastic polyester moulding composition which comprises transesterifying with a saturated aliphatic or cycloaliphatic diol, a dialkyl ester of a low molecular weight aliphatic alcohol, with, as 45 acid component, an aromatic dicarboxylic acid,

and subjecting the ester thus formed to melt condensation and subsequent solid phase condensation to a reduced specific viscosity value as hereinafter defined, of from 0.9 to 2.0 dl/g, 50 wherein there is added, during transesterification or at the beginning of or in the course of melt condensation,

a) from 0.02 to 2% by weight, preferably from 0.05 to 0.6% by weight, calculated 55 on the dialkyl ester used, of inert inorganic solid material having a particle size of less than 5 μ , and
 b) from 0.02 to 0.3% by weight, calculated 60 on the dialkyl ester used, of one or more epoxides of the general formula



in which up to three of the radicals R, R', R'' and R''' may represent hydrogen, and the others, which may be the same or different, 65 each represents an alkyl, cycloalkyl, aryl or aralkyl group, optionally containing ether oxygen, and wherein one of these groups contains an additional epoxide group.

The acid component of the dialkyl ester in 70 the transesterification step optionally also contains up to 10% by weight, calculated on the total weight of dicarboxylic acid, of an aliphatic dicarboxylic acid.

British Patent No. 805,504 describes a process 75 for the preparation of high molecular weight polyesters, in which epoxides are added prior to polycondensation. Those materials are not suitable, however, for being processed into crystalline injection-moulded parts, because the crystallization times are too long to be technically useful and the injection-moulded parts adhere to the walls of the mould. If a mineral crystallization-promoting 80

[Price 25p]

agent, for example, calcium carbonate, is powdered on to the polyester granules, sufficiently short crystallization times can, indeed, be obtained; however, the injection-moulded articles are extremely brittle and have insufficient impact strength. The same result becomes evident, if the order of addition is reversed, i.e. the mineral is added during melt condensation, while the epoxide is applied on to the finished granules by rolling prior to injection-moulding. The present invention reveals the surprising fact that the addition of *both* components prior to, or during, polycondensation not only guarantees a sufficiently fast crystallization of the polyester moulding composition in the mould, but also provides shaped articles having a good impact strength. The shaped articles manufactured in accordance with the invention show excellent mould release properties, even with short dwell times in the mould, and this is important for the economy of the process. Another advantage of the process of the invention is that solid phase condensation of the polyester granules can be carried out more rapidly and thus more carefully with regard to the polyester. Ease of release from the mould and increased speed of solid phase condensation can be obtained by adding even very small amounts of epoxide compound in accordance with the invention. If, for example, polyethylene terephthalate is prepared by adding to the melt, subsequent to the transesterification of dimethyl terephthalate with ethylene glycol, 0.2% by weight of sodium fluoride as nucleating agent and 0.2% by weight of the bis-glycidyl ether of bisphenol A as epoxide compound, a polyester moulding composition is obtained by means of subsequent melt condensation and solid state condensation which exhibits excellent injection-moulding properties, and which imparts the desired mechanical properties to the finished product.

In the preparation of the polyester a dialkyl ester of a low molecular weight aliphatic alcohol for example a dimethyl ester, with an aromatic dicarboxylic acid, for example terephthalic acid, is reacted with a diol, for example ethylene glycol, and the bishydroxy-alkyl esters thus obtained are then subjected to polycondensation, while the excess diol is removed by distillation. The transesterification step is, of course, well known in the manufacture of polyester compositions. By the term "dialkyl ester of a low molecular weight aliphatic alcohol", there is meant a dialkyl ester which is of low enough molecular weight to be suitable for the transesterification step. As is well known, the dimethyl ester is generally used for this purpose. According to this principle, it is also possible to prepare modified polyethylene terephthalate containing besides terephthalic acid, other aromatic or aliphatic dicarboxylic acids as structural units, for example, isophthalic acid, naphthalene 2, 6, dicarboxylic acid or adipic acid, provided that an aliphatic dicarboxylic acid should only be present in an amount of up to 10% by weight. Moreover, modified polyethylene terephthalates can be prepared which contain, besides ethylene glycol, other aliphatic diols, such as neopentyl glycol or butane 1, 4 diol, as alcoholic components. Hydroxy-carboxylic acids may also be used to modify polyethylene terephthalate. Melt condensation is preferably carried out until a RSV value of from 0.6 to 1.1 dl/g is obtained (the RSV value being measured with a solution of 1% by weight in phenol and tetrachlorethane 60:40 at 25°C).

During transesterification, or prior to, or in the course of melt condensation, one or more epoxides are added to the reaction mixture in accordance with the invention, for example, ethylene glycol diglycidyl ether, butanediol-(1,4)-diglycidyl ether, neopentyl glycol diglycidyl ether, 1,4 - dimethylol - cyclo - hexane - diglycidyl ether, 1 - vinyl - cyclo - hexene - 3-diepoxyde, 1,2 - divinyl - cyclo - hexane - diepoxyde, hexadiene - (1,5 - diepoxyde, or the bisglycidyl ether of hydroquinone, resorcinol or bisphenol A. The bisglycidyl ether of bisphenol A is preferably used, preferably in an amount of from 0.15 to 0.25% by weight. The epoxide compounds used are purified by distillation.

Inorganic nucleating agents, such as talcum, kaolin, titanium dioxide, aluminium oxide, pyrophyllite, sodium fluoride, or boron nitride, can be added to the melt during transesterification or polycondensation, in the same way as the epoxide compound: NaF and BN are particularly preferred as nucleating agents. The inorganic nucleating agent can be introduced into the melt at the same time as the epoxide compound, or separately.

The RSV value of granules obtained after the discharge of the melt is increased by means of solid phase condensation. The polyester is required to have a reduced specific viscosity of from 0.9 to 2.0 dl/g. Especially suitable are polyesters having a reduced specific viscosity of from 1.2 to 1.6 dl/g.

In order to keep the absorption of moisture to a low level, the granulated polyester moulding composition may be provided with a coating of an inert hydrophobic substance, for example paraffin or other wax. Such waxes can also improve the rheological properties of the molten moulding composition. Examples of these waxes are neutral or partially neutralized montan wax salts, montan wax ester salts, alkali metal paraffin sulfonates and alkali metal olefin sulfonates.

In order to improve the impact strength, suitable high polymers may be admixed to the polyester composition in known manner, for example, copolymers of ethylene with vinyl acetate, ethylene with acrylic esters or butadiene with styrene.

In general, all steps should be performed under an inert gas atmosphere, i.e. with the exclusion of moisture and oxygen, in order to avoid any impairment of the polyester. The 5 polyester composition preferably contains less than 0.01% by weight of water. The mould is preferably kept at a temperature of at least 100°C; a mould temperature of from 120°C to 150°C is most favourable.

10 The following Examples illustrate the invention, the parts and percentages being by weight.

Example 1

15 1.1 A mixture of 1,000 parts of dimethyl terephthalate, 880 parts of ethylene glycol and 0.31 parts of manganese acetate was slowly brought to a temperature of 225°C, while stirring, while methanol was distilled off by means of a column until the transesterification was completed. By raising the temperature to 270°C, the excess ethylene glycol was separated by distillation. 20 1.2 Parts of the bisglycidyl ether of bisphenol A, 2 parts of boron nitride having an average particle size of 2 microns, and 0.04 parts of a polycondensation catalyst (for example, Sb_2O_3 or GeO_2) were added, and the polycondensation was carried out with an increase of 25 temperature of 275°C and with a final pressure of 0.1 mm of mercury. The finished polyester had a reduced specific viscosity of 0.85 dl/g. After it had been 30 discharged from the reaction vessel, the polyester strand was granulated, and the granules thus obtained were brought to a reduced specific viscosity of 1.50 dl/g by bulk condensation at a temperature of 235°C and a pressure of from 0.1 to 0.2 m of mercury for 8 hours.

35 1.2. The polyester moulding composition thus obtained was moulded into 100 sheets of dimensions 60 × 60 × 2 mm. The following injection-moulding conditions were 40 adjusted: cylinder temperature: 270°C/260°C/260°C; mould temperature: 140°C, injection time: 15 seconds, injection pressure: 140 atmospheres gauge. The dwell time in the mould, was, 45 25 seconds after which all the sheets fell off the mould automatically and showed smooth and glossy surfaces. The density of the sheets was 1.3730 g/cc, their reduced specific viscosity was 1.30 dl/g. The impact strength of the sheets was 50 tested by way of a fall test. For this purpose, 80 sheets were subjected to impact in such a way that a drop hammer sliding on almost frictionless rails was allowed to fall from different heights vertically on to the sheets lying on a frame. The frame had a hole of diameter 26 mm; the drop hammer, which

55 was aligned with the center of the hole, had a spherical top of a diameter of 9 mm. An average height of fall of 115 cm was ascertained for the series of 80 sheets.

Example 2
(Comparative Example)

2.1 The transesterification was effected analogous to Example 1.1. Subsequent to transesterification 4 parts of talcum, as well as 0.04 part of polycondensation catalyst, were stirred into the melt, and the polycondensation was carried out. After the discharge of the polyester material, the strand was granulated, and bulk condensation was effected until an RSV of 1.450 dl/g had been reached. The duration of the bulk condensation was 14 hours. 70

2.2 The moulding composition thus obtained was moulded into sheets, under the same moulding conditions as indicated in Example 1.2. However, in order to obtain fairly satisfactory shaped articles, the residence times in the mould had to be considerably increased. Nevertheless, the sheets stuck to the mould, and their surfaces showed deep impression marks from the ejector pins. With a dwell time of 25 seconds, only 21 of 100 sheets fell off the mould automatically, while the others had to be removed by hand; with a dwell time of 45 sec., 42 of 100 sheets fell off the mould, and with a dwell time of 60 sec., 49 of 100 sheets fell off the mould automatically. With a dwell time of 25 seconds, the reduced specific viscosity of the sheet material was 1.25 dl/g, and the density was 1.365 g/cc. The average 80 height of fall was 106 cm. 90

2.3 The polyester material prepared in accordance with paragraph 2.1., which had been provided with 4 parts of talcum, was rolled for 8 hours with 1.4 parts of 1,4-butanediol diglycidyl ether in a drum with the exclusion of air and moisture. The moulding composition thus obtained was processed into sheets under the same conditions as indicated in Example 1.2. The mould release properties of the sheets which had smooth and glossy surfaces were good; of 100 sheets each, 95 fell off the mould automatically with a dwell time in the mould of 25 seconds. The reduced specific viscosity measured was 1.27 dl/g. However, the average height of fall for 80 sheets was only 28 cm. 100

2.4 The polyester mass prepared in accordance with paragraph 2.1., which had been provided with 4 parts of talcum, was rolled for 8 hours with 1.4 parts of 1,4-butanediol diglycidyl ether in a drum with the exclusion of air and moisture. Subsequently, the granules which had been 105 coated with the epoxide were melted at 110

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265°C, and were then extruded and granulated. After drying until a water content of 0.01% by weight was reached, the injection moulding composition thus obtained was processed into sheets under the same conditions as indicated in Example 1.2. The mould release properties of the smooth sheets were satisfactory; with a dwell time of 25 seconds, 87 of 100 sheets fell off the mould automatically. The reduced specific viscosity measured was 1.22 dl/g; the density was 1.372, and the average height of fall was very low, similar to that of Example 2. 3., i.e., 25 cm.

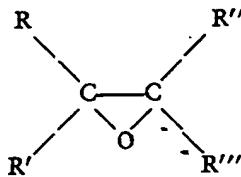
Example 3

3.1 A modified polyethylene terephthalate was prepared in a manner analogous to Example 1.1, except that 2 parts of sodium fluoride having an average particle size of 3 to 4 microns and 1.5 part of glycidyl ether of 1,4-butanediol were added to the melt, subsequent to transesterification. The RSV value of the finished injection moulding composition was 1.52 dl/g after solids condensation.

3.2 The polyester moulding composition thus obtained was moulded into sheets under the same conditions as indicated in 1.2. With a dwell time in the mould of 25 seconds, all 100 sheets fell off the mould automatically and showed smooth and glossy surfaces. The density was ascertained at a temperature of 22°C and was found to be 1.375 g/cc. The reduced specific viscosity was 1.31 dl/g, and the average height of fall for a series of 80 sheets was 92 cm.

WHAT WE CLAIM IS:—

- 40 1. A process for the production of a crystalline thermoplastic polyester moulding composition which comprises transesterifying with a saturated aliphatic or cycloaliphatic diol, a dialkyl ester of a low molecular weight aliphatic alcohol, with, as acid component, an aromatic dicarboxylic acid, and subjecting the ester thus formed to melt condensation and subsequent solid phase condensation to a reduced specific viscosity value as hereinbefore defined, of from 0.9 to 2.0 dl/g, wherein there is added, during transesterification or at the beginning of or in the course of melt condensation,
 - 55 a) from 0.02 to 2% by weight, calculated on the dialkyl ester used, of inert inorganic solid material having a particle size of less than 5 μ , and
 - 55 b) from 0.02 to 0.3% by weight, calculated on the dialkyl ester used, of one or more epoxides of the general formula
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- 80
- 85
- 90
- 95
- 100
- 105
- 110
- 115



in which up to three of the radicals R, R', R'' and R''' may represent hydrogen, and the others, which may be the same or different, each represents an alkyl, cycloalkyl, aryl or aralkyl group, optionally containing ether oxygen, and wherein one of these groups contains an additional epoxide group.

2. A process as claimed in claim 1, wherein the acid component of the dialkyl ester in the transesterification step also contains up to 10% by weight, calculated on the total weight of dicarboxylic acid, of an aliphatic dicarboxylic acid.

3. A process as claimed in claim 2, wherein the aliphatic dicarboxylic acid is adipic acid.

4. A process as claimed in any one of claims 1 to 3, wherein there is also present during the transesterification step a hydroxycarboxylic acid.

5. A process as claimed in any one of claims 1 to 4, wherein the aromatic dicarboxylic acid is terephthalic acid.

6. A process as claimed in claim 4, wherein the terephthalic acid is used in admixture with isophthalic acid or naphthalene 2,6-dicarboxylic acid.

7. A process as claimed in any one of claims 1 to 6, wherein the saturated diol is ethylene glycol.

8. A process as claimed in claim 7, wherein the ethylene glycol is used in admixture with neopentyl glycol or butane 1,4-diol.

9. A process as claimed in any one of claims 1 to 8, wherein the amount of inert inorganic solid material added is from 0.05 to 0.6% by weight, calculated on the dialkyl ester.

10. A process as claimed in any one of claims 1 to 9, wherein talcum, kaolin, titanium dioxide, aluminium oxide or pyrophyllite is used as inert inorganic solid material.

11. A process as claimed in any one of claims 1 to 9, wherein sodium fluoride or boron nitride is used as inert inorganic solid material.

12. A process as claimed in any one of claims 1 to 11, wherein the epoxide constituent is one or more of: ethylene glycol diglycidyl ether, butane-diol-1,4-diglycidyl ether, neopentyl glycol diglycidyl ether, 1,4-dimethyloxy-cyclohexane-diglycidyl ether, 1-vinyl-cyclohexene-3-diepoxide, 1,2-divinyl-cyclohexane-diepoxide, hexadiene(1,5)-diepoxide, or the bisglycidyl ether of hydroquinone or resorcinol.

13. A process as claimed in any one of claims 1 to 11, wherein the bisglycidyl ether of bisphenol A is used as the epoxide.

14. A process as claimed in claim 13, wherein the amount of bisglycidyl ether of bisphenol A is from 0.15 to 0.25% by weight, calculated on the dialkyl ester used.

5 15. A process as claimed in claim 1, wherein polyethylene terephthalate is prepared by the transesterification of dimethyl terephthalate with ethylene glycol, followed by melt and solid phase condensation of the ester so formed, and wherein there is added, subsequent to the transesterification, 0.2% by weight of sodium fluoride as nucleating agent and 0.2% by weight of the bis-glycidyl ether of bisphenol A.

10 16. A process as claimed in any one of claims 1 to 15, wherein the melt condensation process is carried out until the polyester has an RSV value as hereinbefore defined of from 0.6 to 1.1 dl/g.

15 17. A process as claimed in any one of claims 1 to 16, wherein the solid phase condensation process is carried out until the polyester has an RSV value of from 1.2 to 1.6 dl/g.

20 18. A process as claimed in any one of claims 1 to 17, carried out under an inert gas atmosphere.

25 19. A process as claimed in any one of claims 1 to 18, carried out with the exclusion of moisture to such an extent that the mould-

ing composition obtained contains less than 0.01% by weight of water.

20. A process as claimed in any one of claims 1 to 19, wherein the moulding composition obtained is subsequently moulded at a mould temperature of at least 100°C.

35 21. A process as claimed in claim 20, wherein the mould temperature is from 120°C to 150°C.

22. A process as claimed in claim 1, conducted substantially as described in Example 1 or Example 3 herein.

40 23. A crystalline thermoplastic polyester moulding composition, whenever prepared by a process as claimed in any one of claims 1 to 22.

24. A crystalline thermoplastic polyester moulding composition as claimed in claim 23, in the form of granules coated with an inert hydrophobic substance.

45 25. An injection-moulded article whenever obtained from a crystalline thermoplastic polyester moulding composition as claimed in claim 23 or claim 24.

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